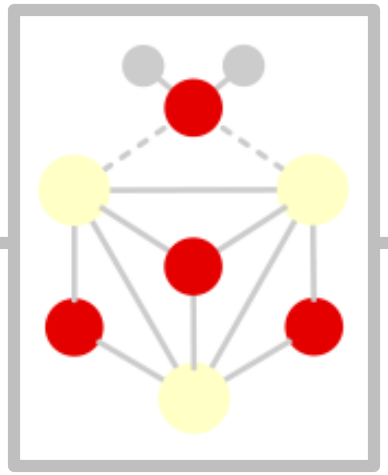


Interrogation of $MoO_yC_nH_n^-$ chemifragments illuminates Mo–(η^2–acetylene) interactions within $Mo_xO_y^-$ and ethylene reactions

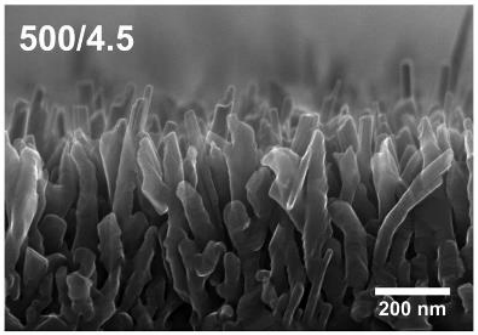
Josey Topolski
C. C. Jarrold Group
Indiana University

ISMS, June 19, 2018

Molybdenum Oxide Catalysts

Benefits of MoO_3

Low cost
Nontoxic
Environmentally benign
High stability



SEM micrograph of the molybdenum oxide film cross section deposited at [T]/[P].

Inzani, K. *Phys. Chem. Chem. Phys.* **2017**, 19, 9232.

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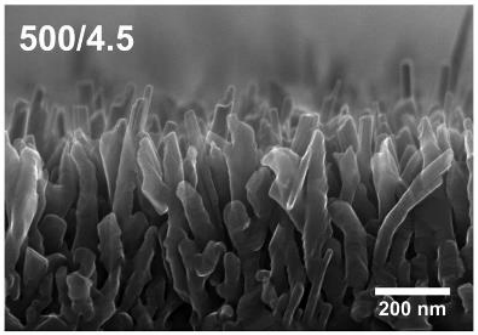

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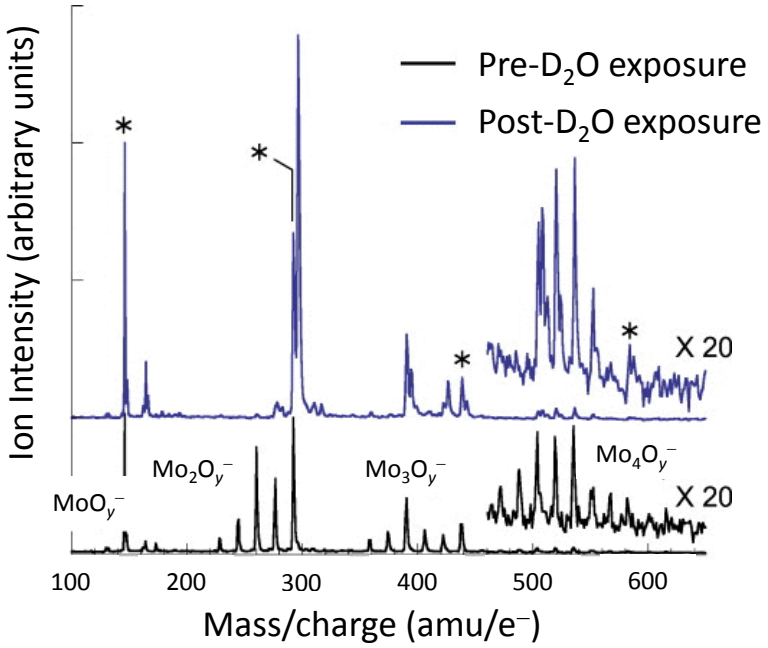
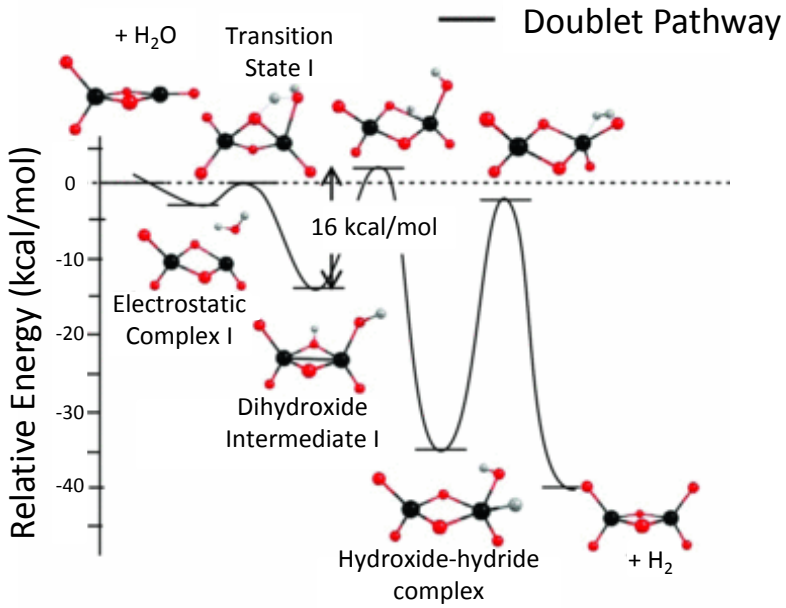
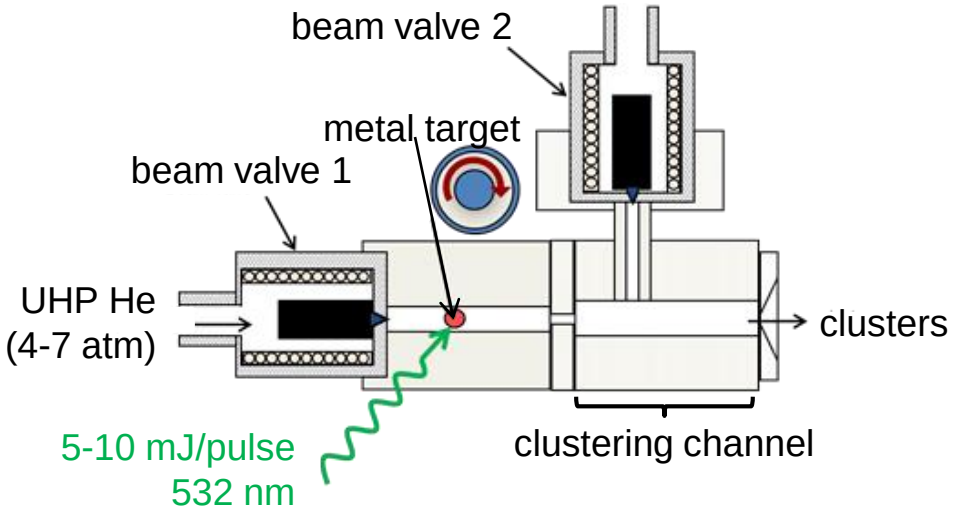


Rothgeb, D. W. *J. Chem. Phys.* **2010**, 133, 054305.



Ray, M. *J. Chem. Phys.* **2014**, 141, 104310.

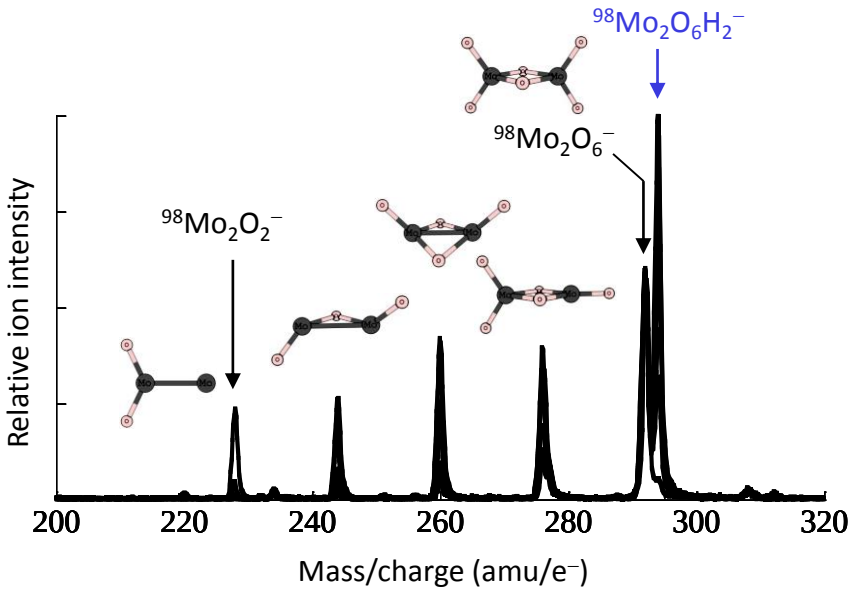
Production of Clusters



D.P. = Diffusion Pump; T.P. = Turbo Pump

$Mo_xO_y^-$ Clusters and H_2 Production

$$Mo_xO_y^- + H_2O \rightarrow Mo_xO_{y+1}^- + H_2$$



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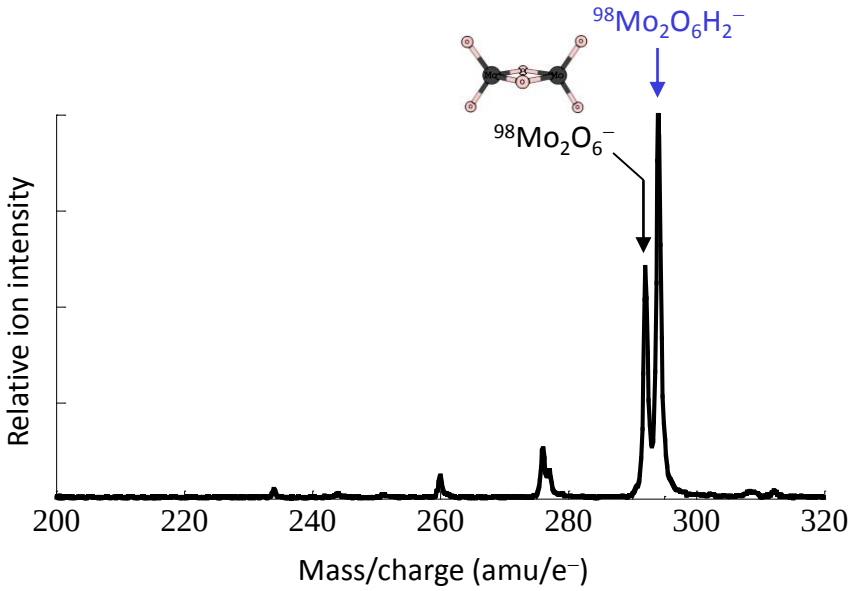
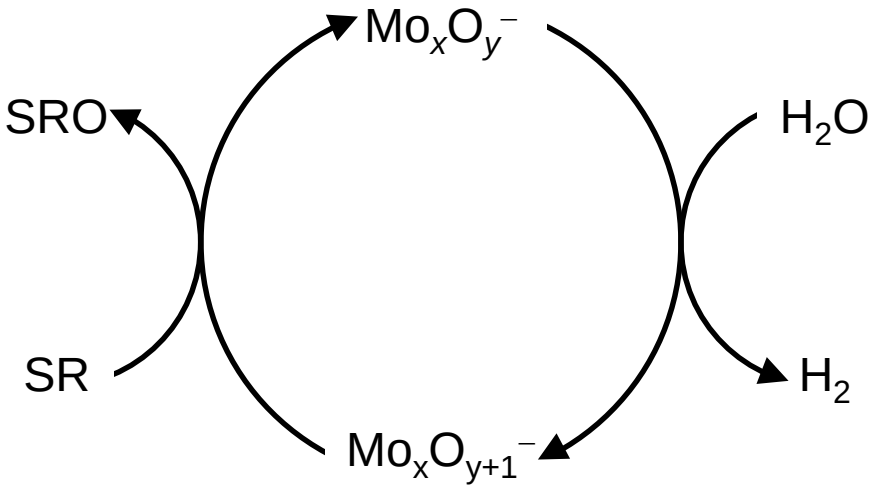


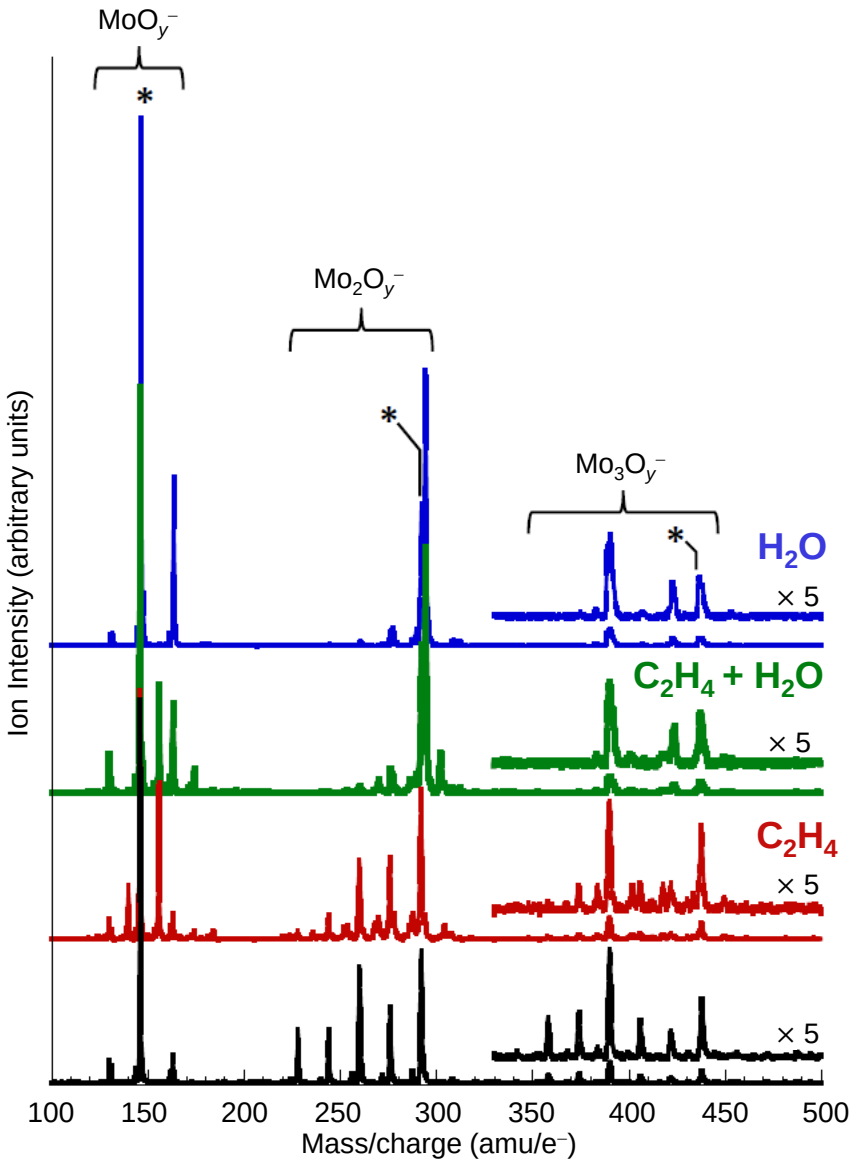
Sacrificial Reagent for a Complete Catalytic Cycle



SR = C_2H_2, C_2H_4

Rothgeb, D. W. *J. Chem. Phys.* **2010**, 133, 054305.

$Mo_xO_y^- + H_2O + C_2H_4$



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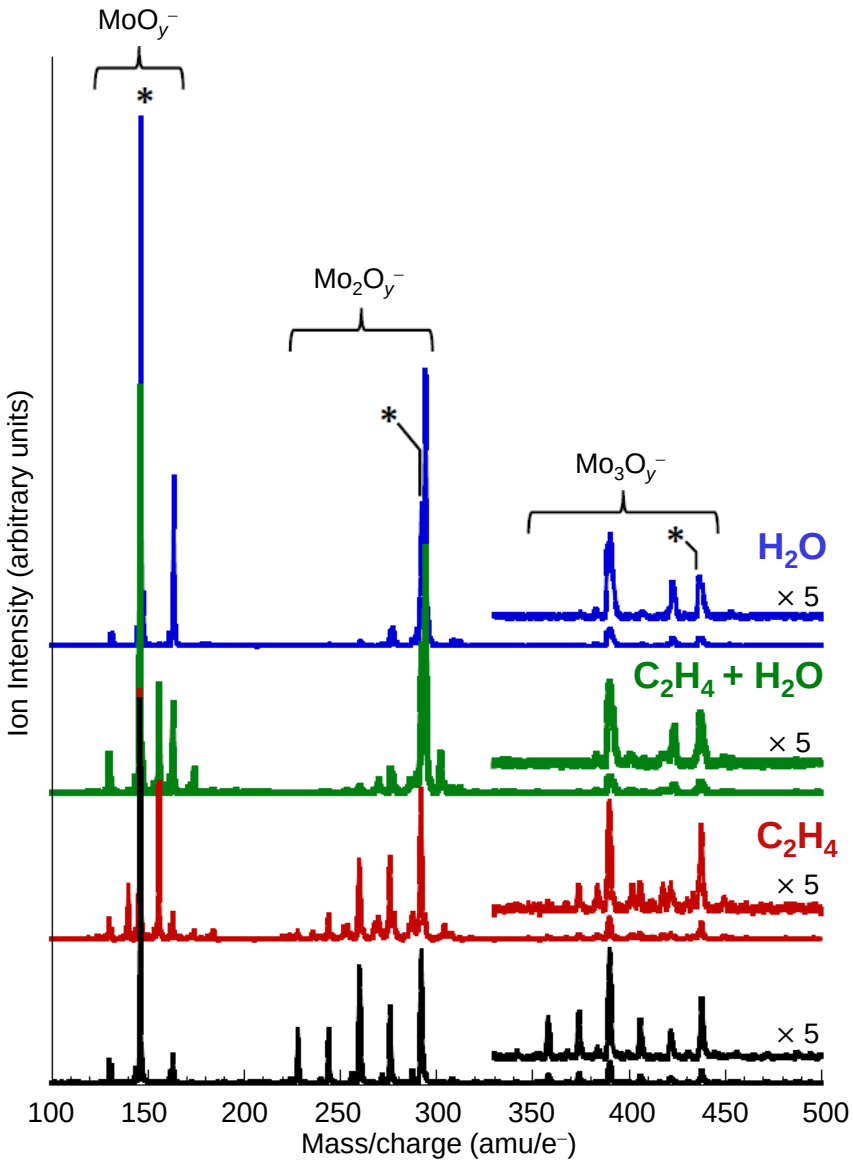

Multitude of Side Reactions

$$Mo_2O_2^- + C_2H_4 \rightarrow MoOC_2H_2^- + MoOH_2$$
$$\rightarrow MoO_2C_2H_2^- + MoH_2$$
$$\rightarrow Mo_2O_2C_2H_2^- + H_2$$

$$Mo_2O_2^- + 2\ C_2H_4 \rightarrow MoO_2C_2H_2^- + MoC_2H_6$$
$$\rightarrow MoO_2C_4H_6^- + MoH_2$$
$$\rightarrow Mo_2O_2C_2H_2^- + C_2H_6$$

$$Mo_2O_3^- + C_2H_4 \rightarrow MoO_2C_2H_2^- + MoOH_2$$
$$\rightarrow Mo_2O_3C_2H_2^- + H_2$$

$$Mo_2O_3^- + 2\ C_2H_4 \rightarrow MoO_2C_2H_2^- + MoOC_2H_6$$
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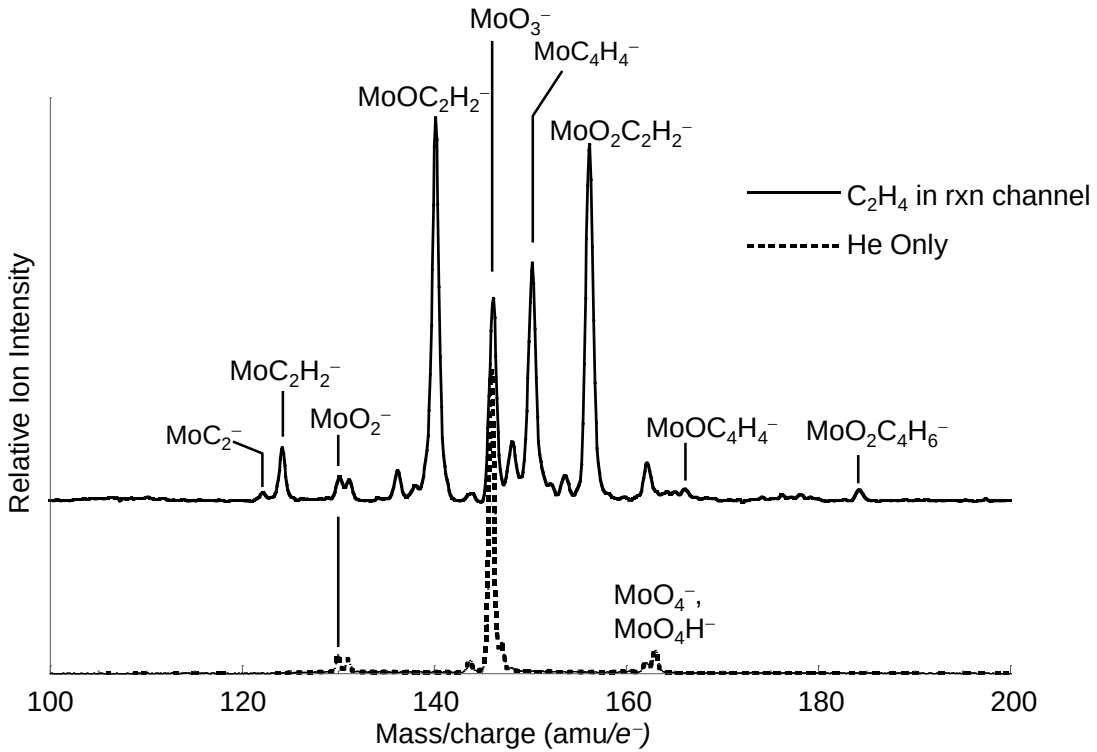
$$\rightarrow Mo_2O_4C_2H_4^-$$

$$Mo_2O_4^- + 2\ C_2H_4 \rightarrow Mo_2O_4C_2H_2^- + C_2H_6$$
$$Mo_2O_4^- + C_2H_4 + H_2O \rightarrow Mo_2O_5C_2H_2^- + 2\ H_2$$
$$Mo_2O_4^- + 2\ C_2H_4 + H_2O \rightarrow Mo_2O_5C_2H_2^- + C_2H_6 + H_2$$

Chemifragmentation to form $MoO_yC_nH_m^-$



<u>No</u> Mo^- or MoO^- Precursors!

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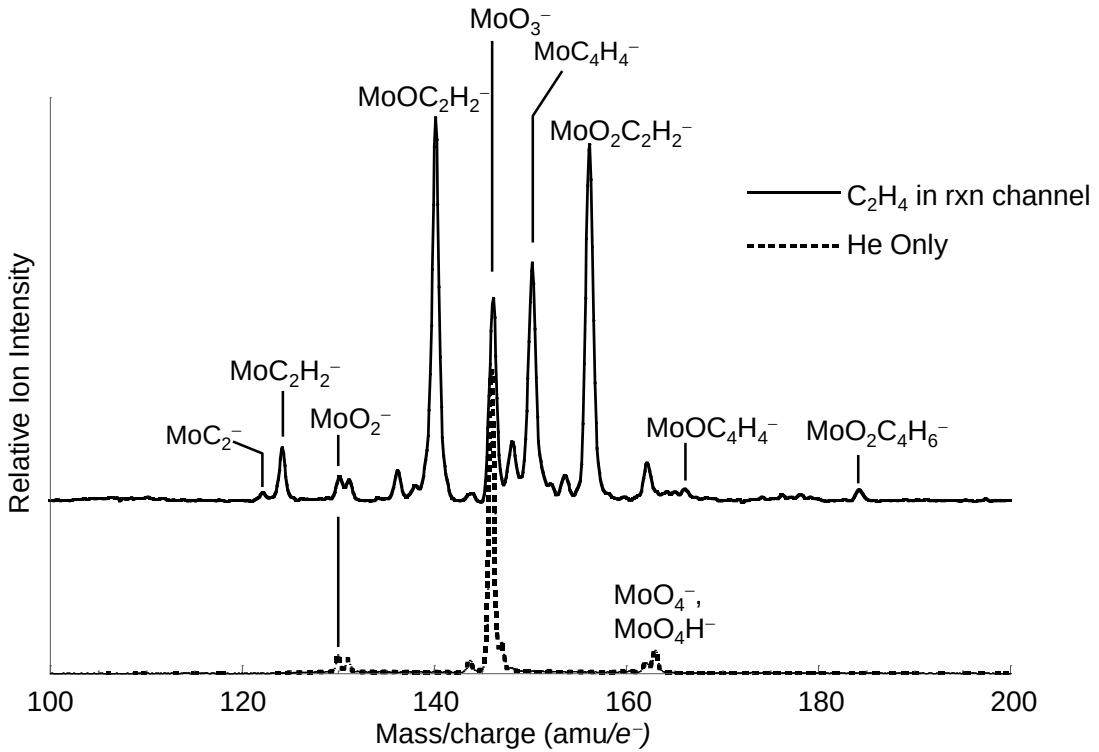

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<u>Examples of Possible Chemifragmentation Reactions</u>

$Mo_2O_2^- + C_2H_4 \rightarrow \mathbf{MoOC_2H_2^-} + MoOH_2$
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$Mo_2O_3^- + C_2H_4 \rightarrow \mathbf{MoO_2C_2H_2^-} + MoOH_2$

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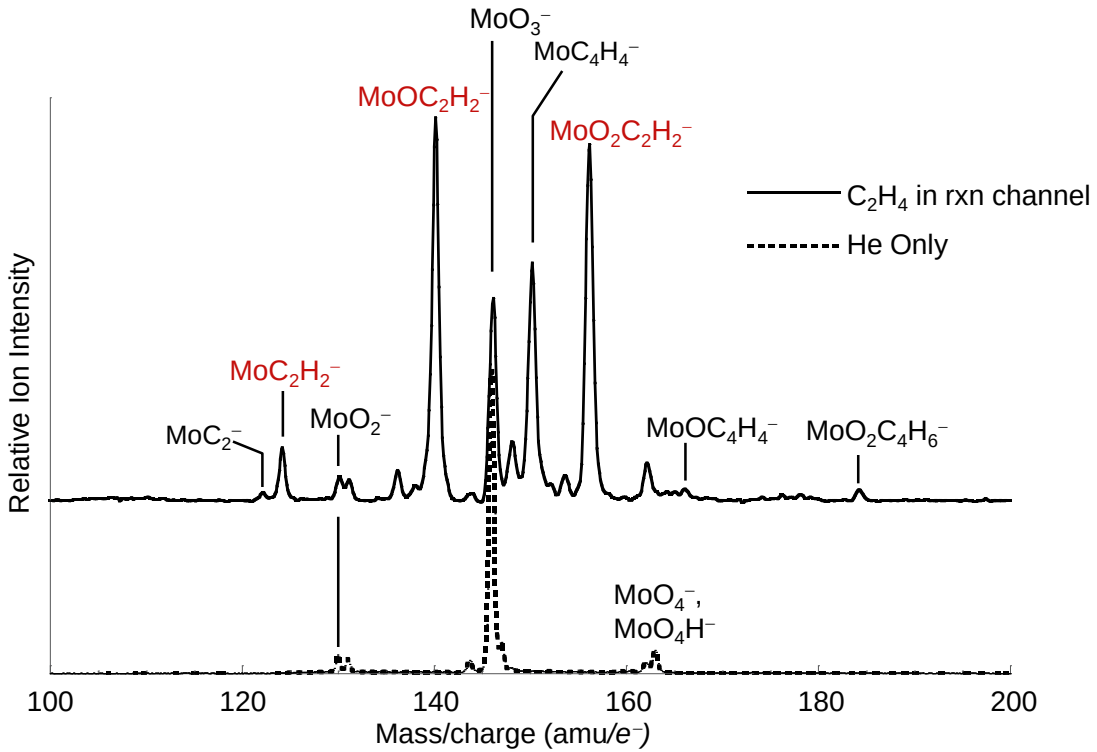

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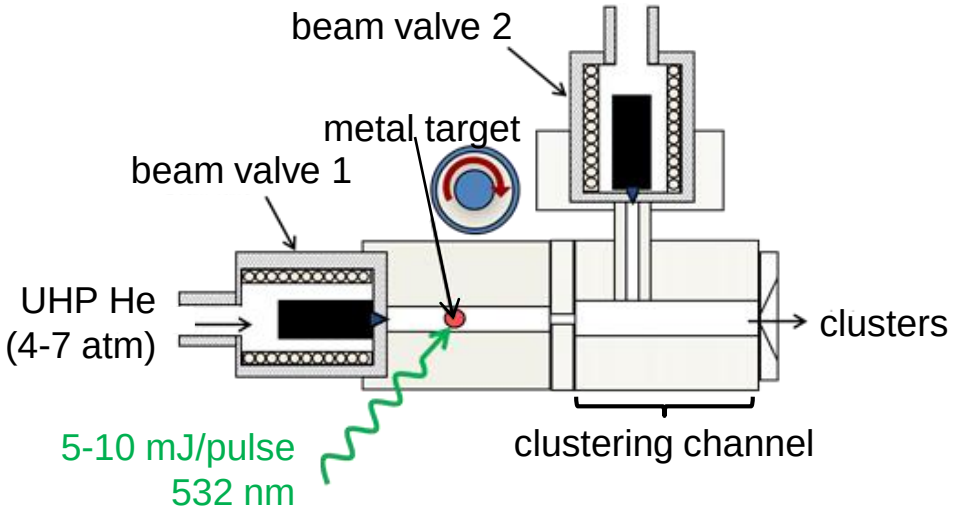

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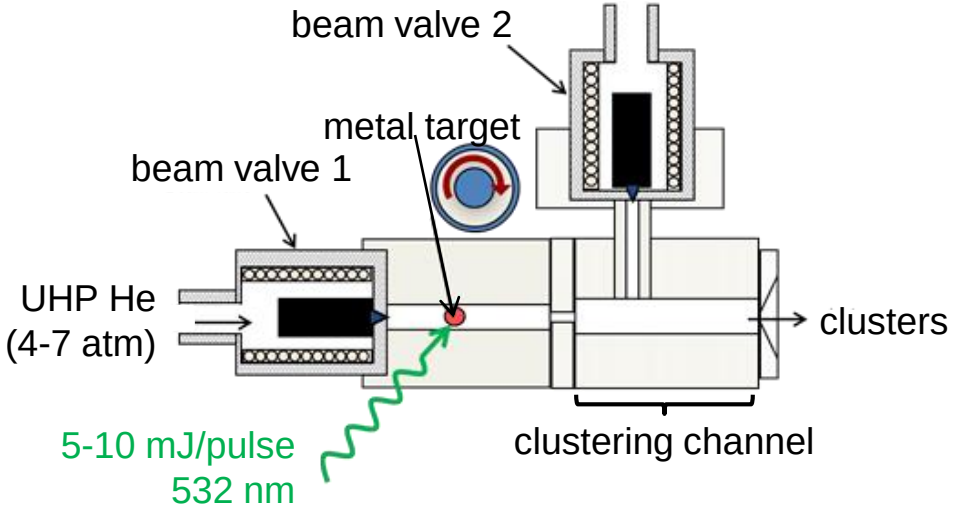


$$e^{-}BE = h\nu - e^{-}KE$$

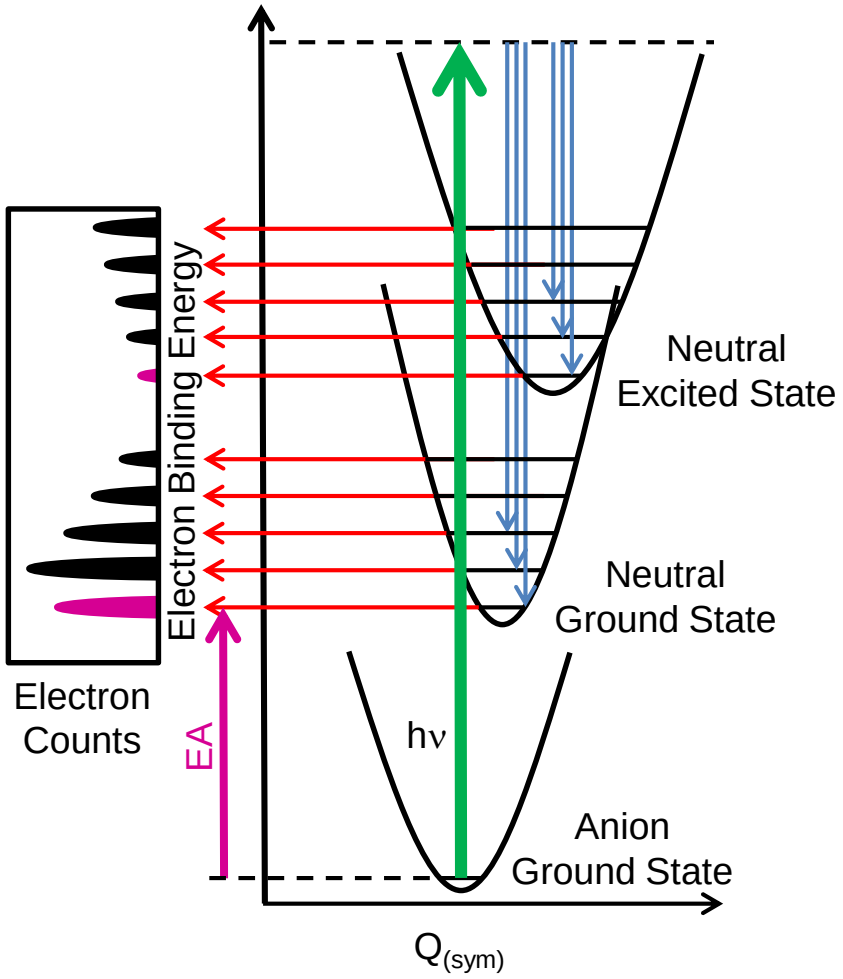
D.P. = Diffusion Pump; T.P. = Turbo Pump

Principles of Anion PE Spectroscopy

$$A^- + h\nu \longrightarrow \mathrm{A} + e^-$$

$$e^- KE = h\nu - EA_A + E_{int}^- - E_{int}^0$$

$$E_{int} = E_{electronic} + E_{vibrational} + E_{rotational}$$



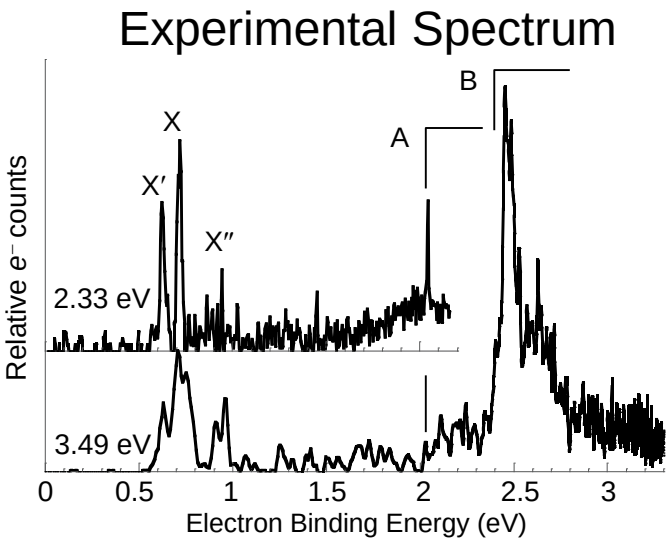
Spin Selection Rule:

$$\Delta s = \pm {}^1/_2$$

Franck – Condon Principle:

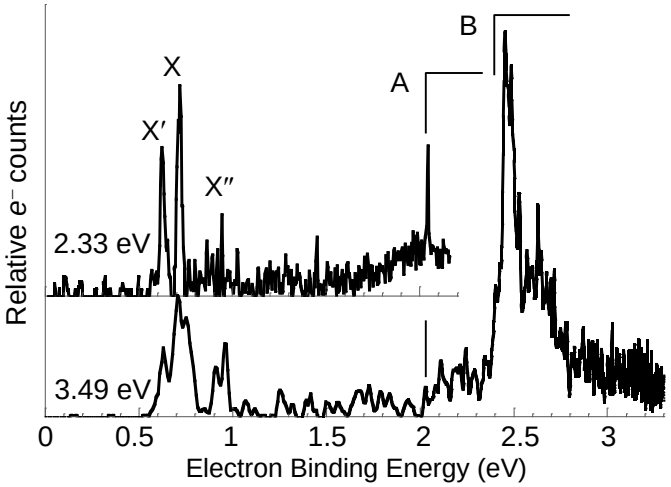
$$I_{v''\rightarrow v'} \propto |< \Psi'_{vib} | \Psi''_{vib} > |^2$$

$MoC_2H_2^-$

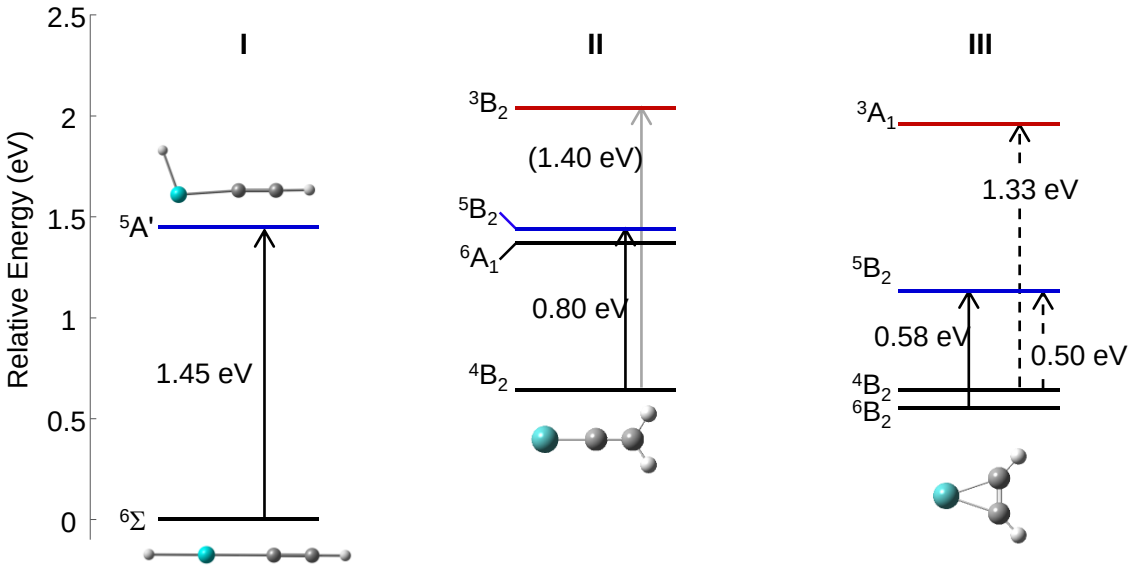

Experimental Spectrum
B
X
A
X′
X″
2.33 eV
3.49 eV
Relative e⁻ counts
0
0.5
1
1.5
2
2.5
3
Electron Binding Energy (eV)

$MoC_2H_2^-$

Experimental Spectrum



Calculated Structures and Spectra

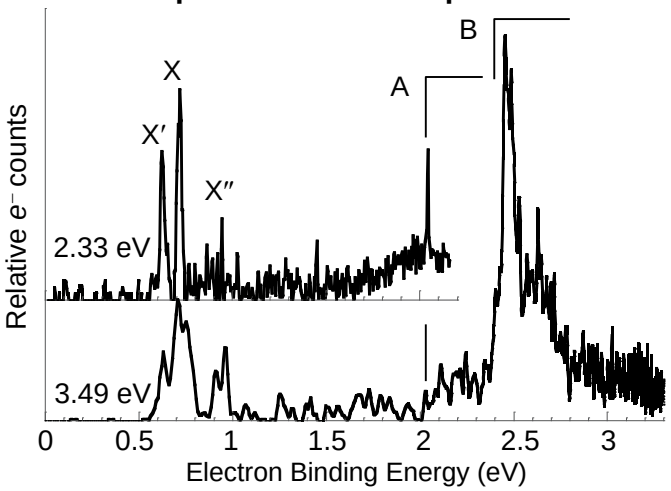


Richard Schaugaard

Calculations: uB3LYP/def2-SVPP optimization, CCSD(T) single-point

$MoC_2H_2^-$

Experimental Spectrum



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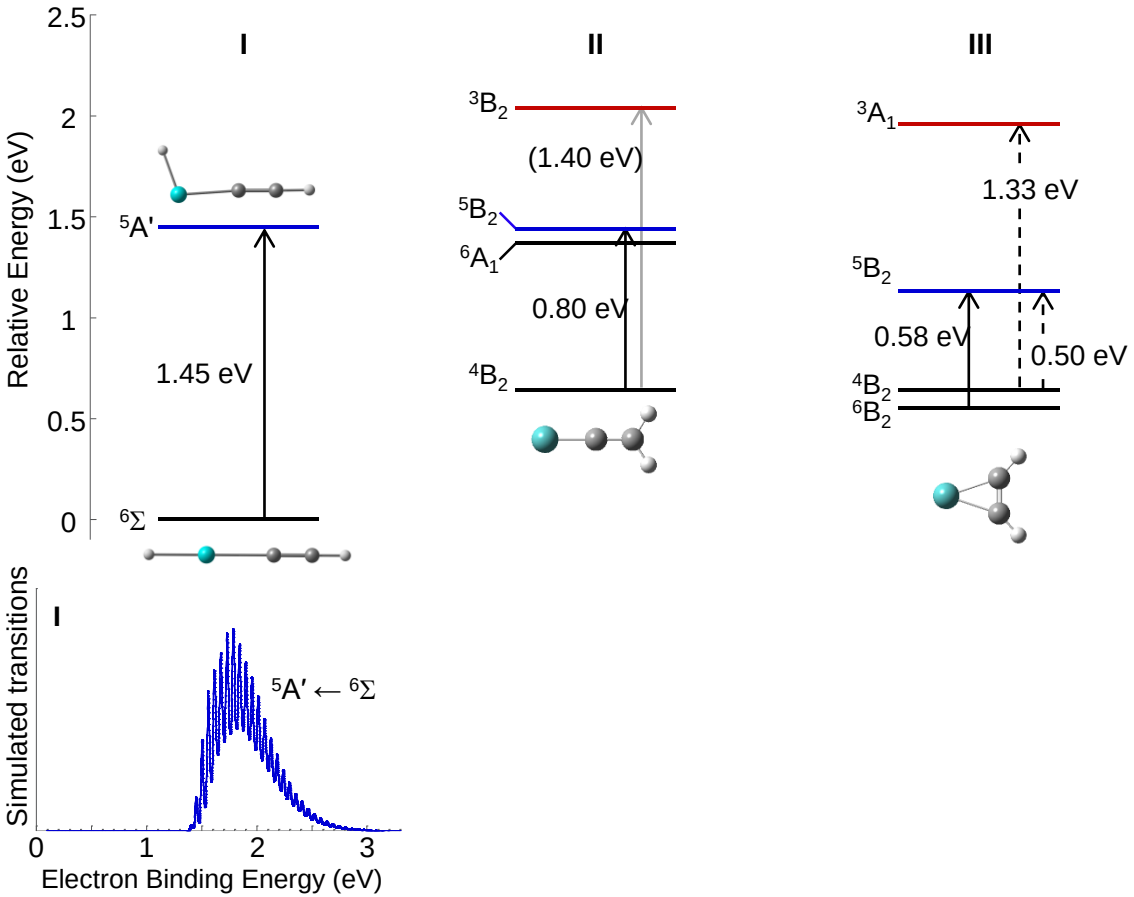

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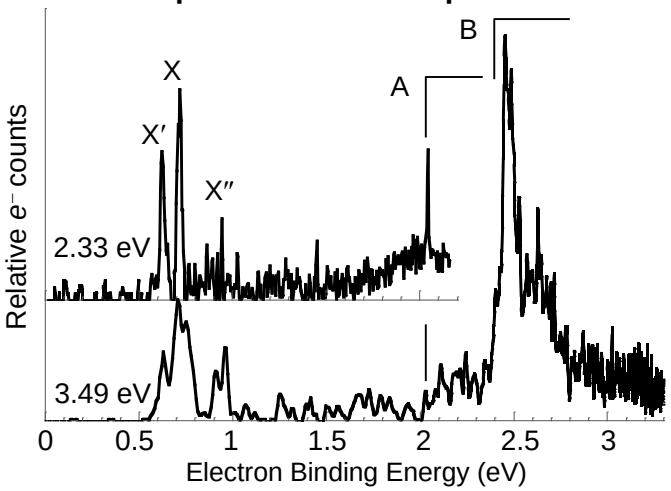

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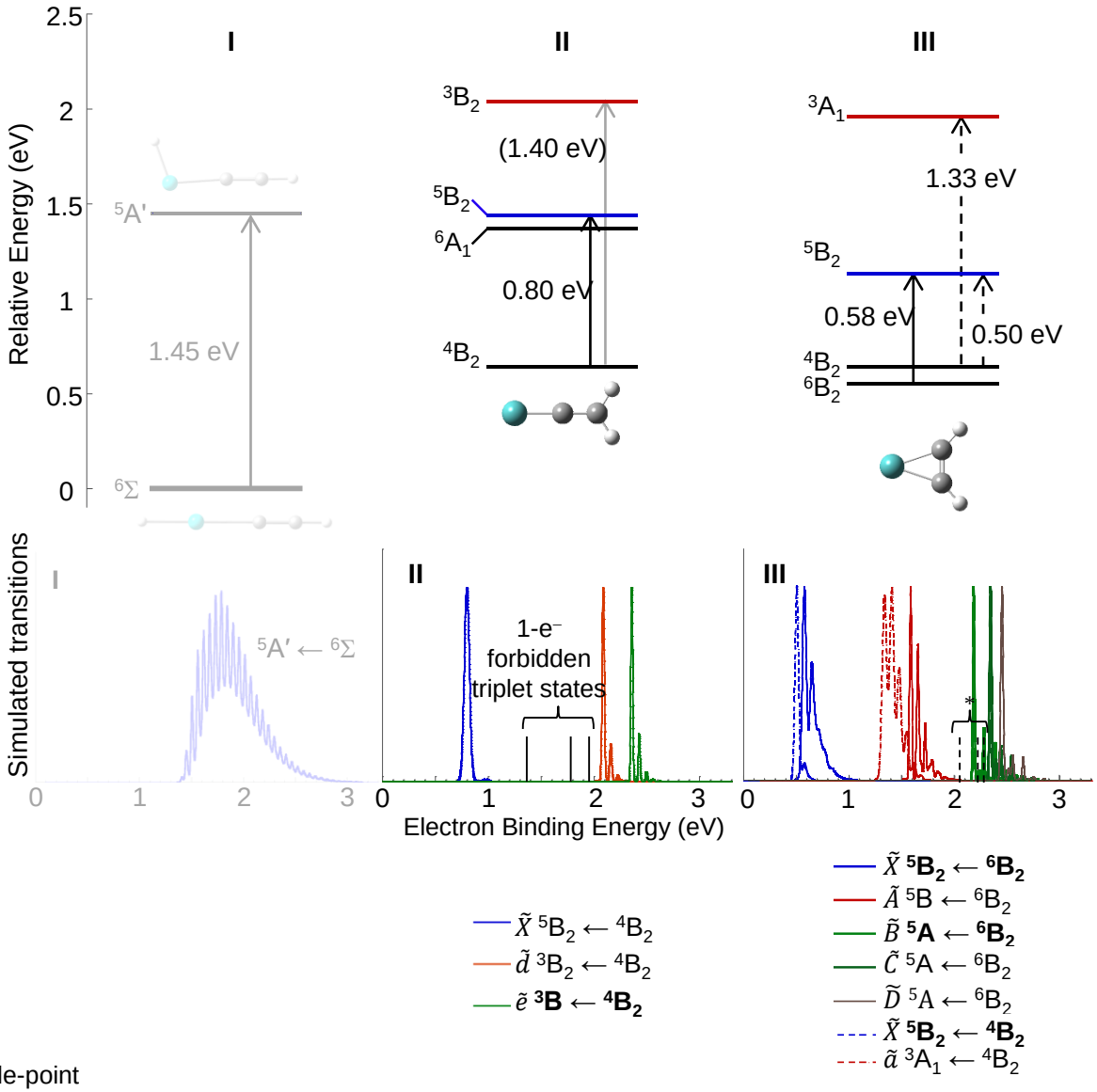

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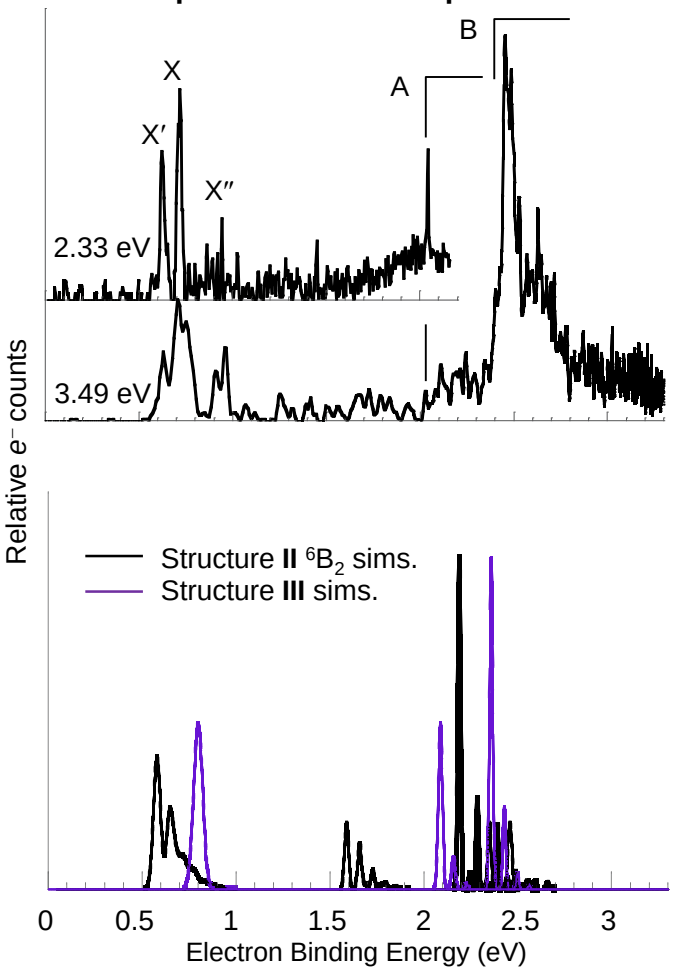

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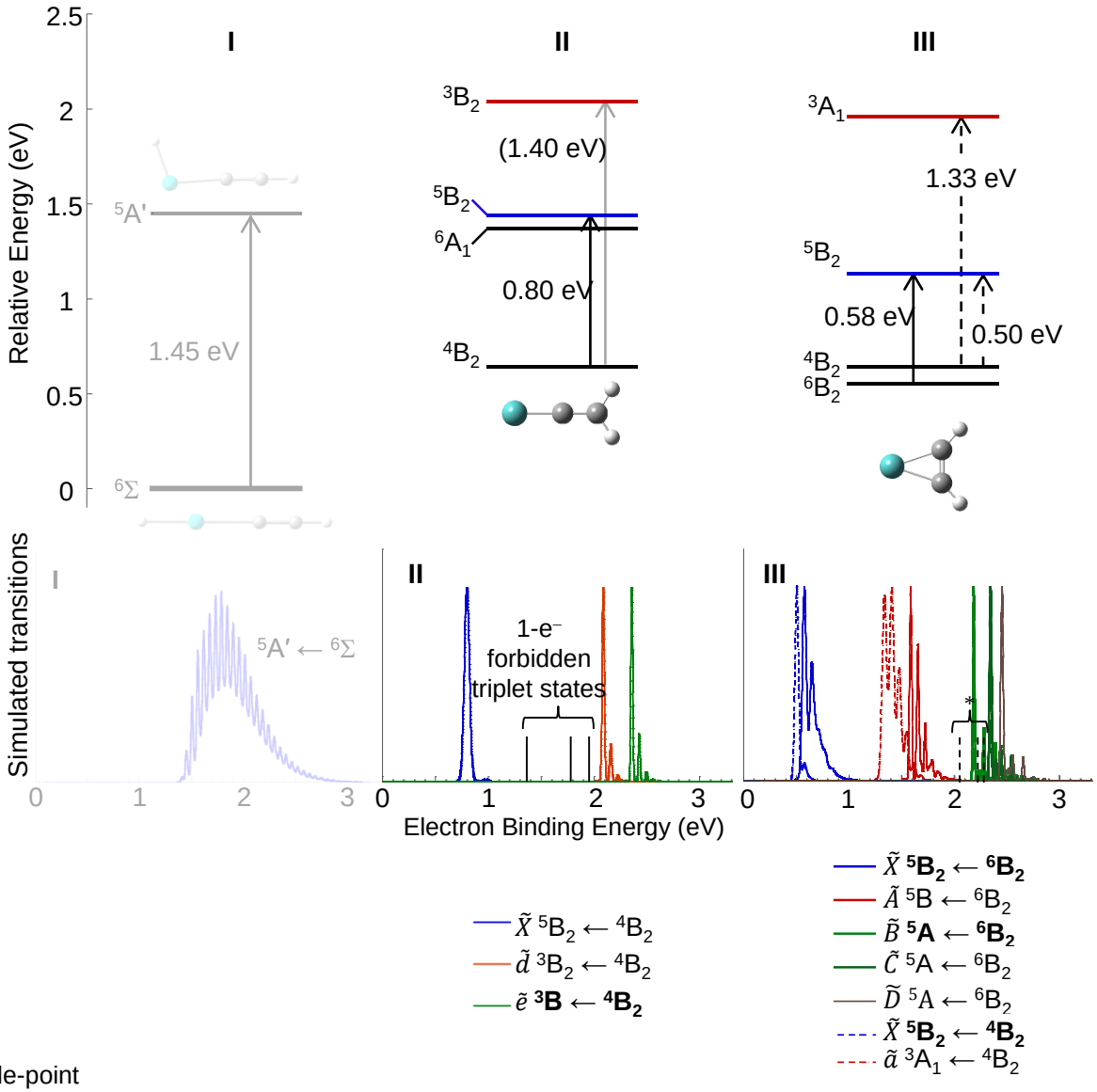

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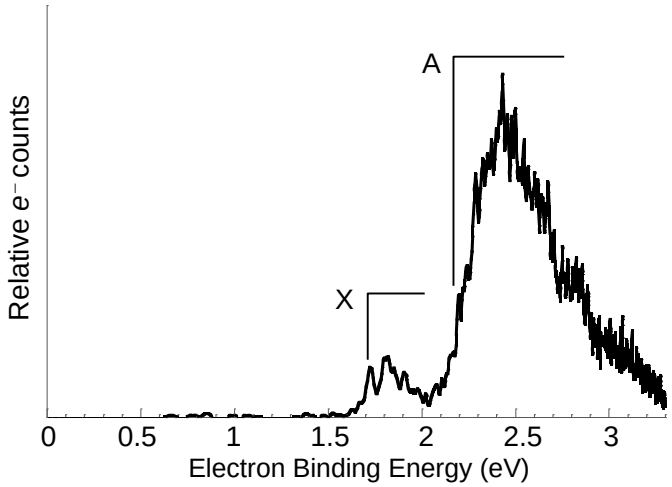

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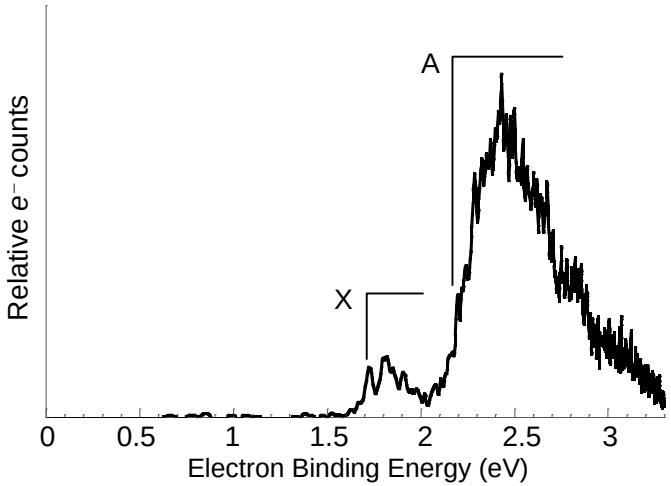

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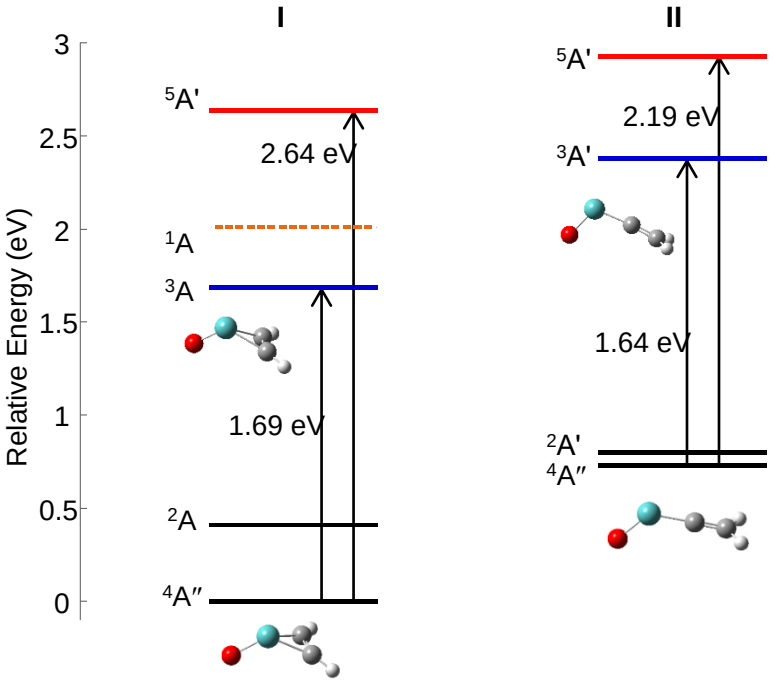

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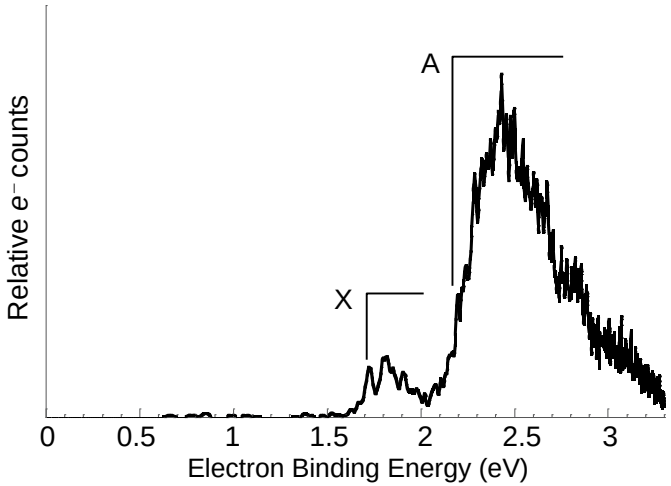

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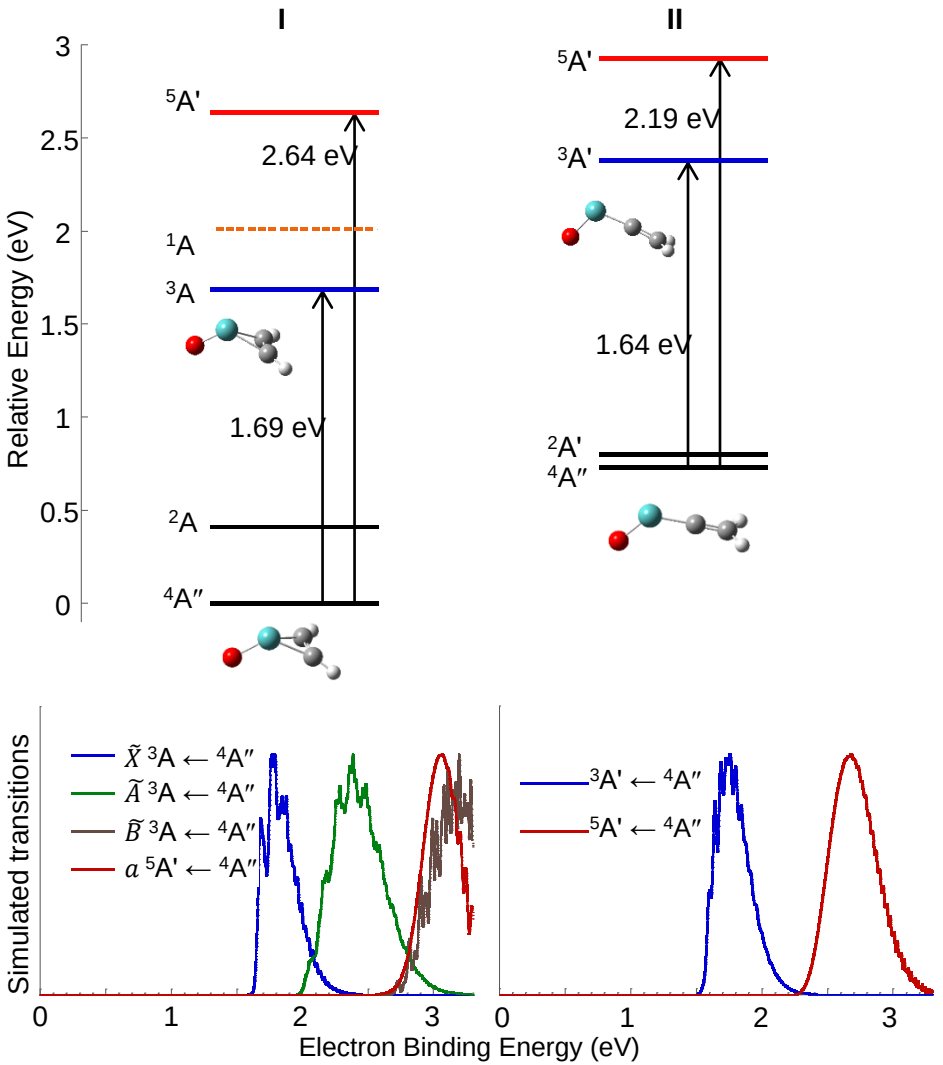

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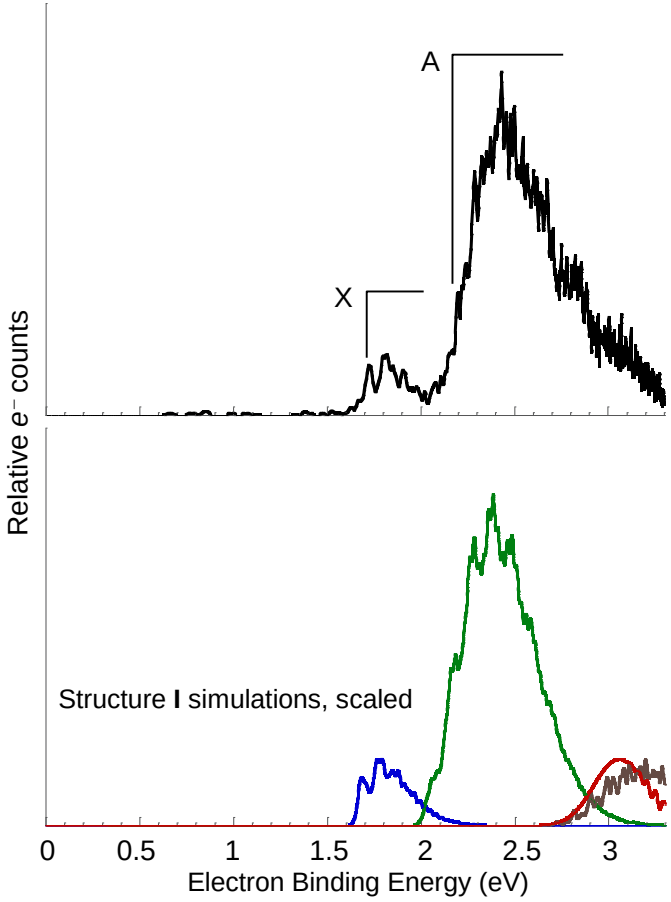

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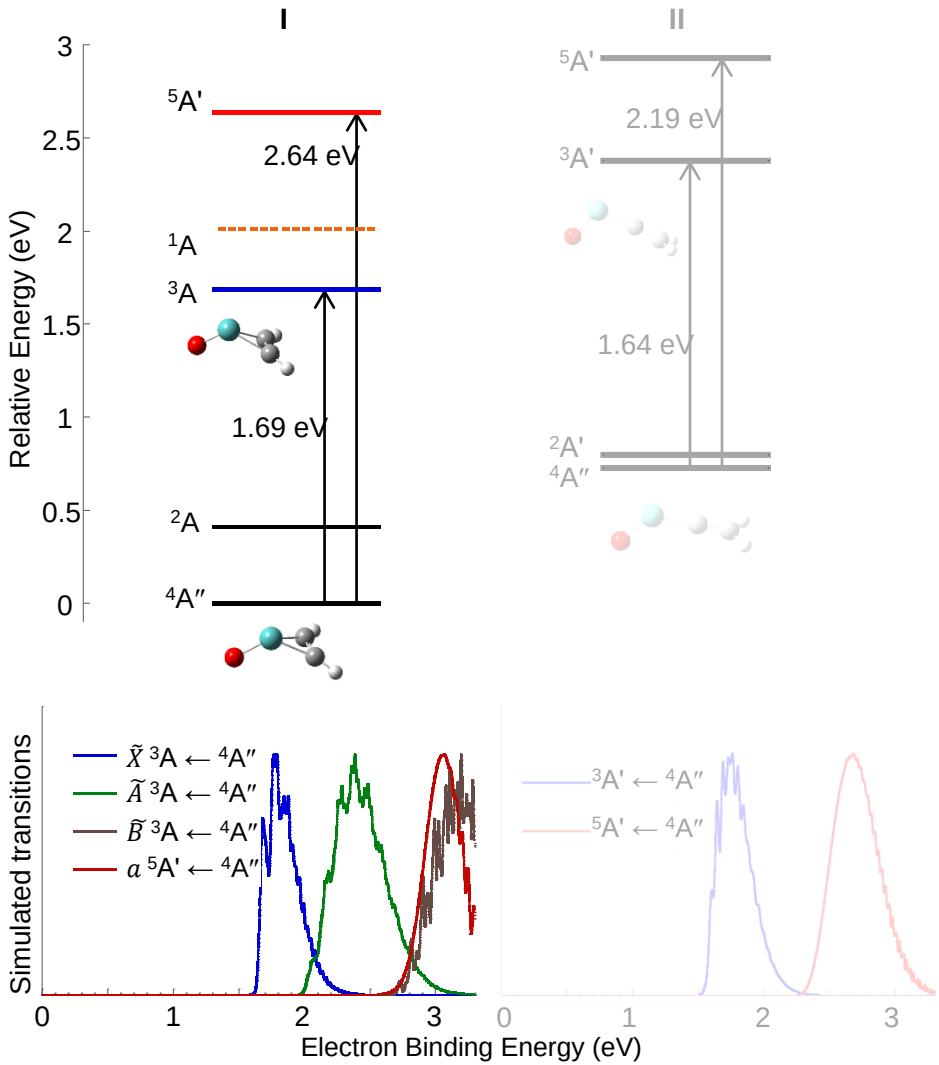

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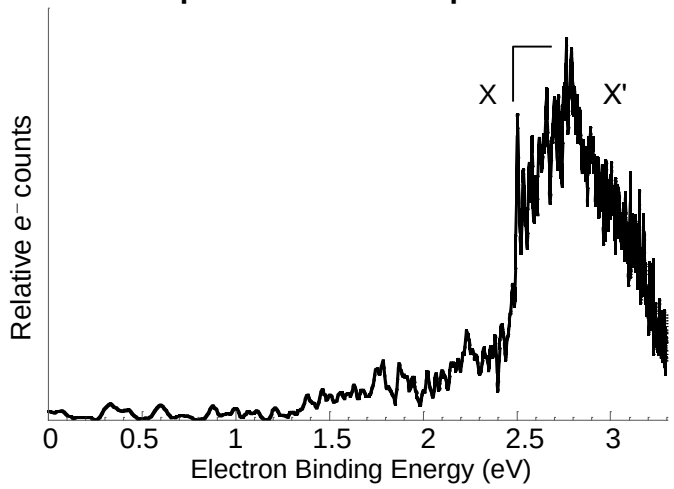

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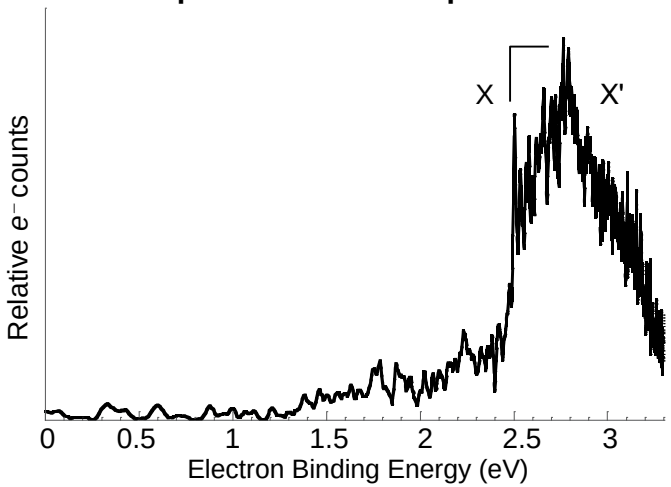
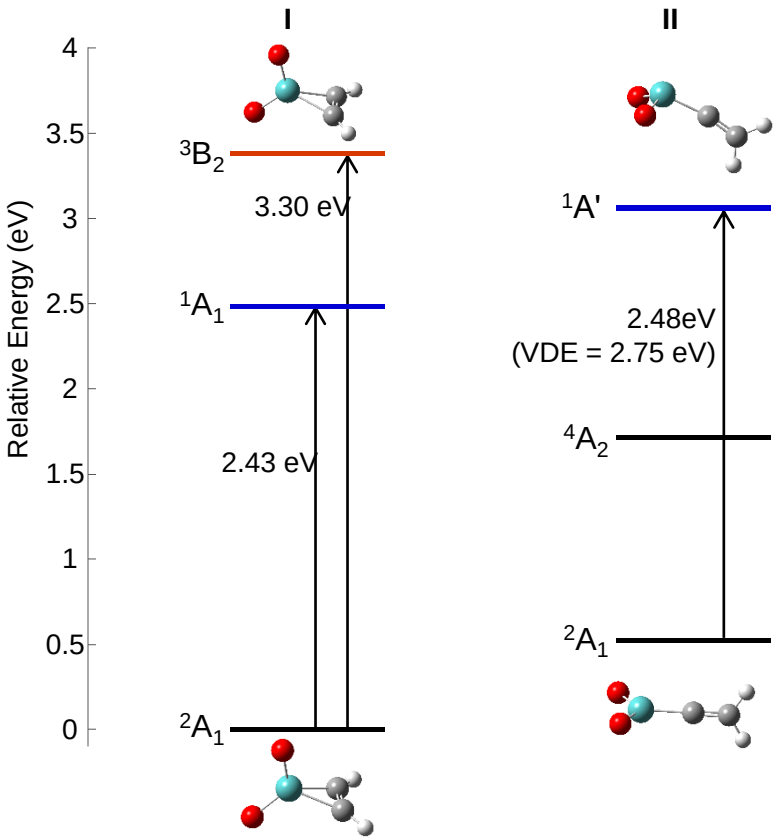


Calculated Structures



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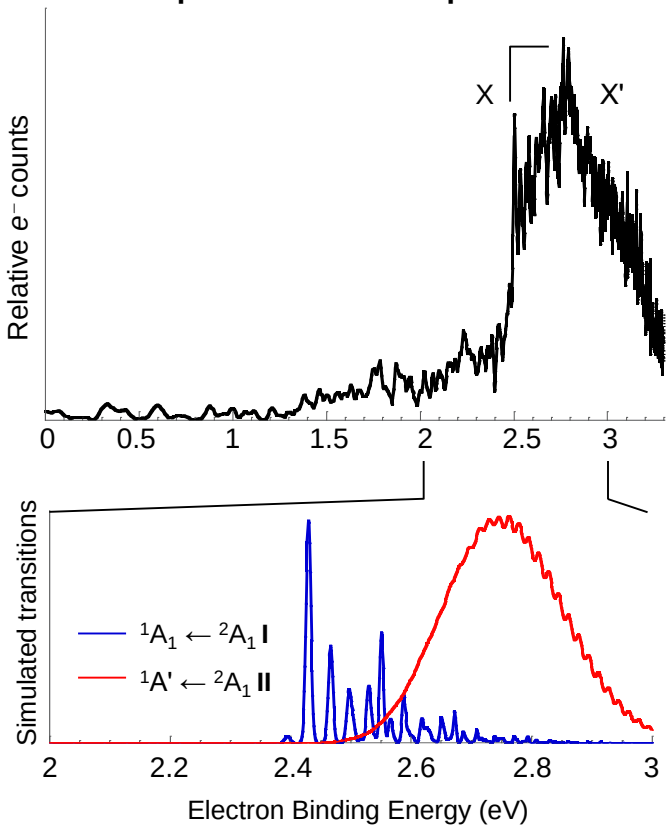

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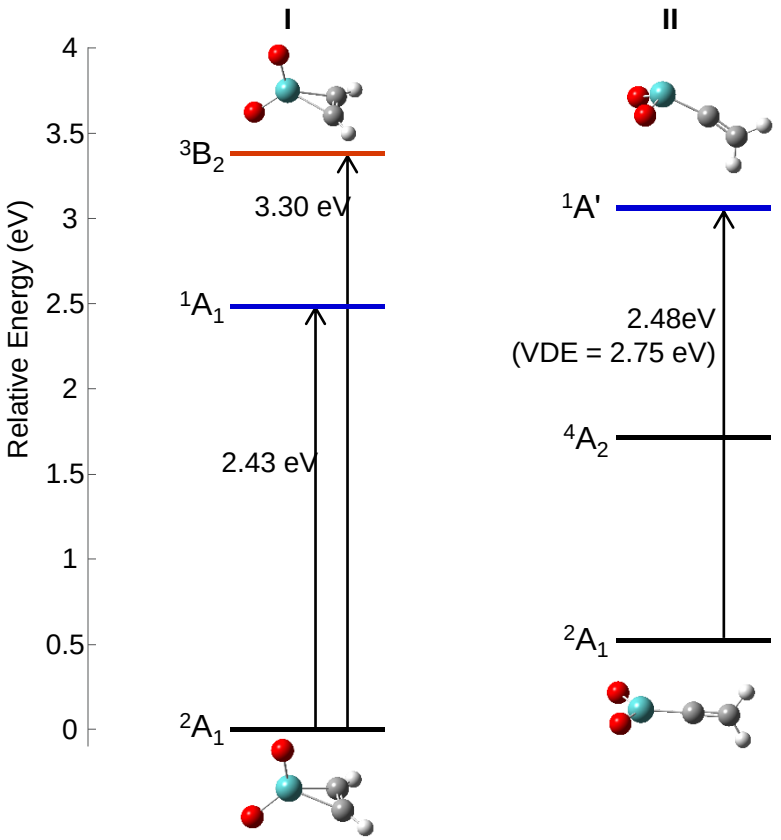

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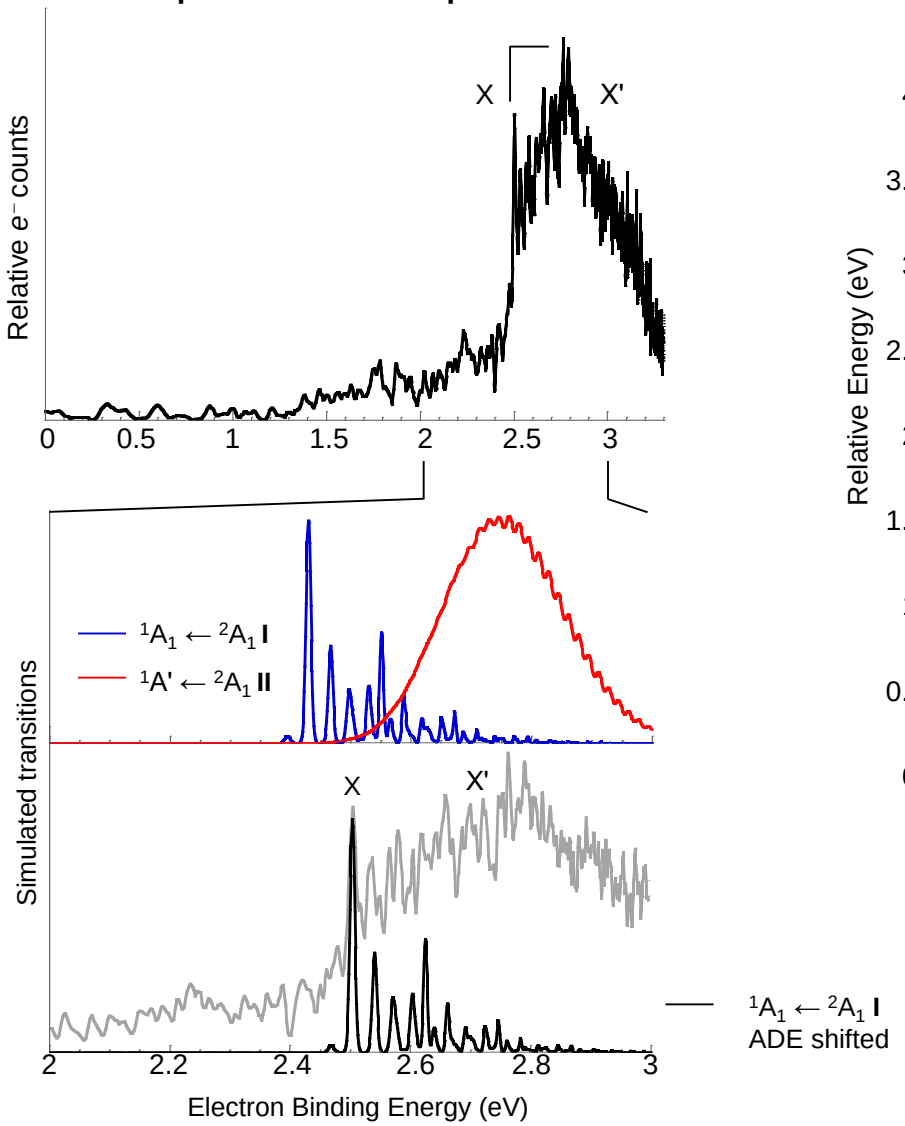

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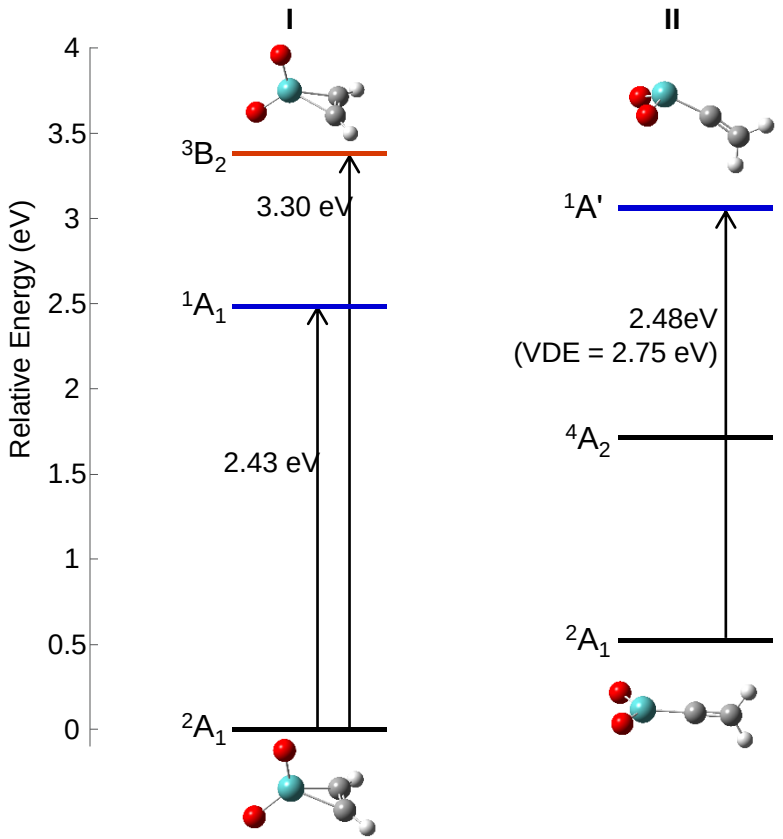

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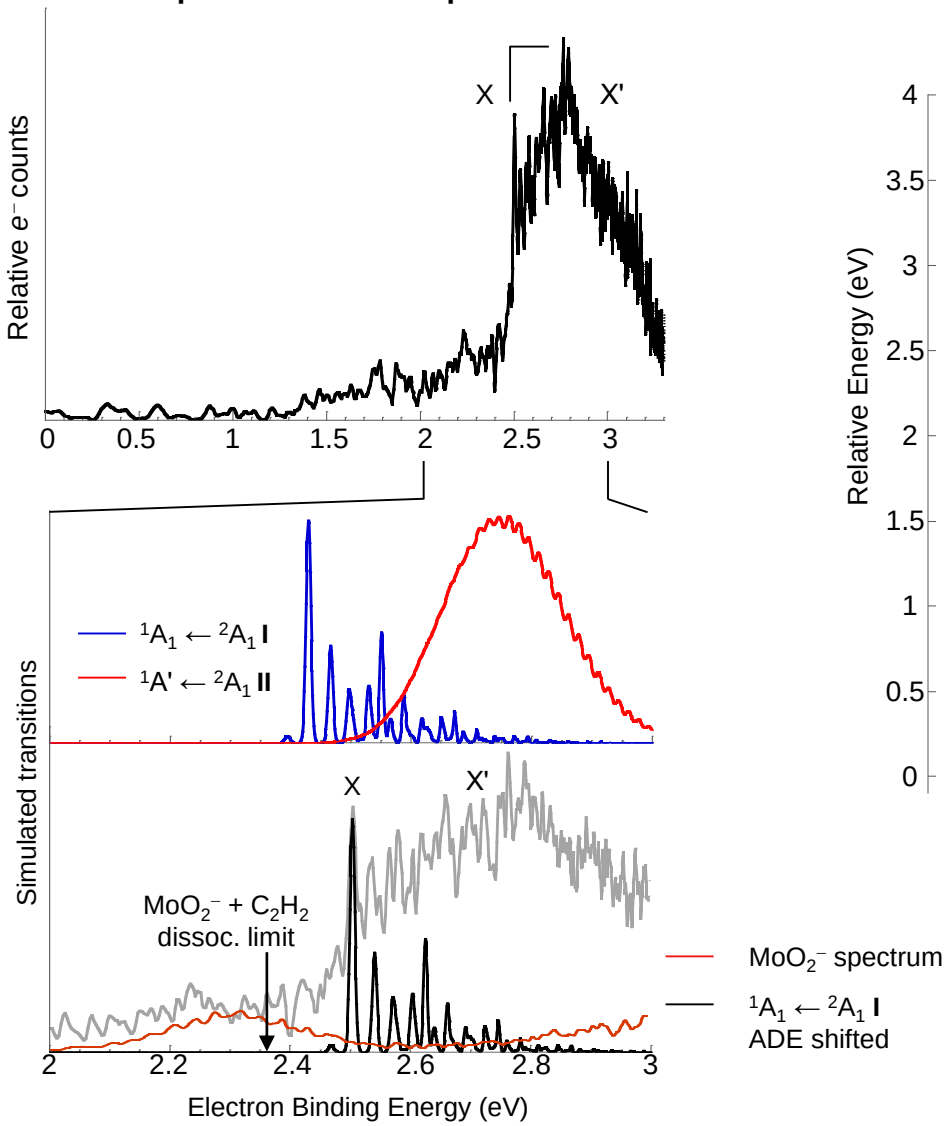

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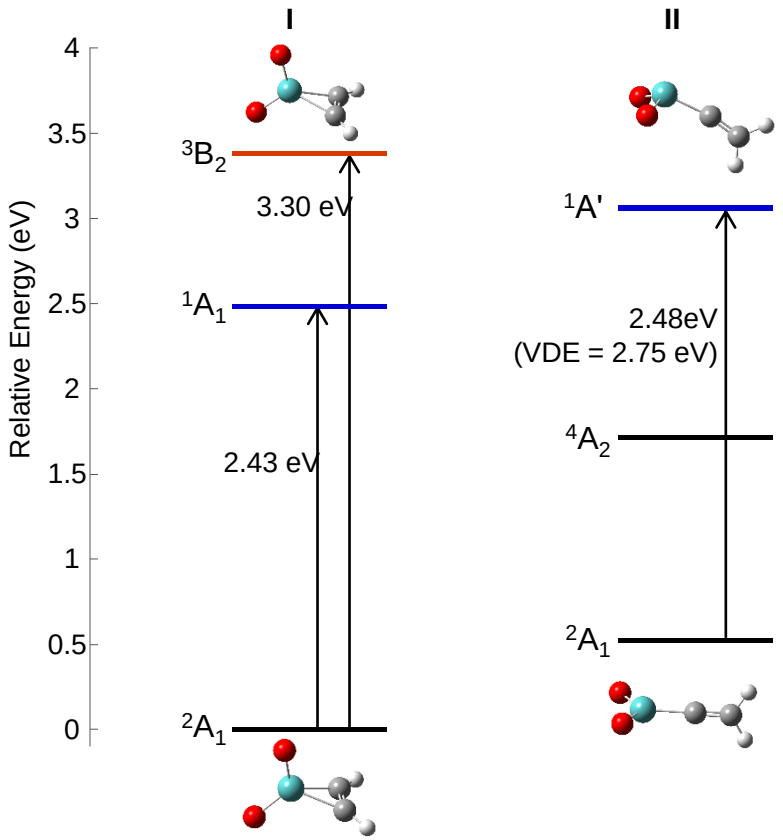

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Take-Away Points

- Monometallic species are formed via chemifragmentation of larger clusters
- Many of these chemifragment complexes feature C_2H_2 units
- η^2–acetylene complexes are consistent with the experimental PES
  BUT the vinylidene complexes cannot be definitively ruled out

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- η^2–acetylene complexes are consistent with the experimental PES
  BUT the vinylidene complexes cannot be definitively ruled out

And a Little Perspective

- Ethylene isn't reactive with all metal oxide clusters…
  i.e. $Nb_xO_y^-$ and $Ta_xO_y^-$
- Chemifragmentation products have been seen before…
  i.e. $Mo_xO_y^-$ + CH_4 or C_2H_6

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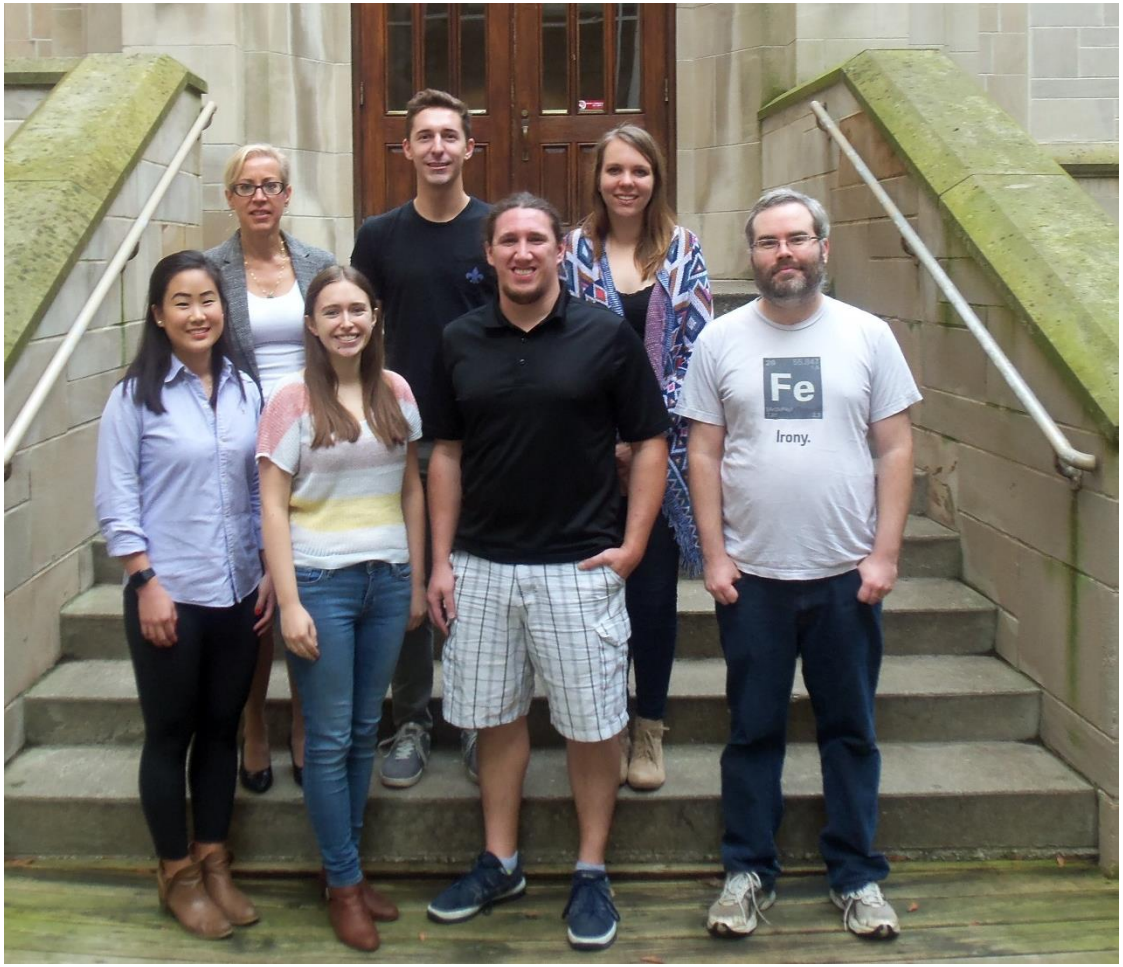

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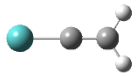
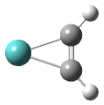
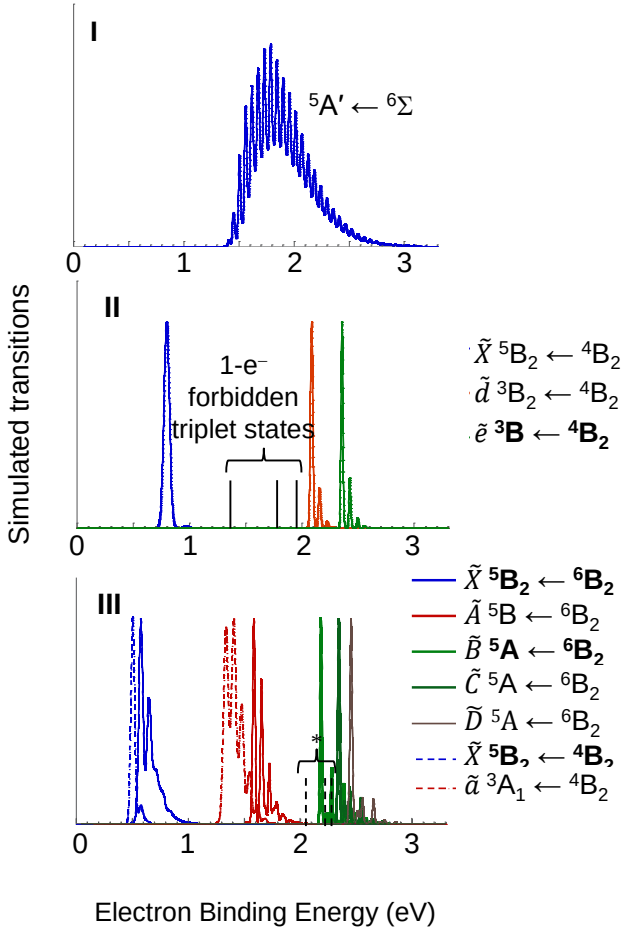
Angular Distribution

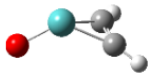
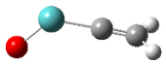
$$\frac{d\sigma}{d\Omega} = \frac{\sigma_{total}}{4\pi}\left[1 + \frac{\beta}{2}(3cos^2\theta - 1)\right]$$

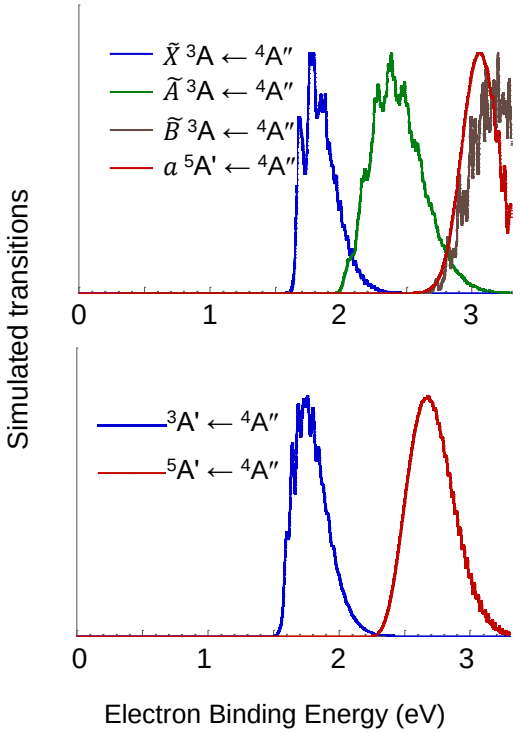
$-1 \leq \beta \leq 2$

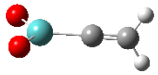
	Transition	ω″ (cm^{-1})	ω′ (cm^{-1})	ΔQ (Å·$amu^{1/2}$)	
$MoC_2H_2^-$ Structure **I** 	$^5A' \leftarrow {}^6\Sigma$ Origin = 1.45 eV T = 300 K	1374	1836	0.21	C-C stretch
		329	495	0.52	Bend with Mo-C stretch[1]
		321	425	0.64	Bend with Mo-C stretch[2]
		193	206	0.2	Bend
$MoC_2H_2^-$ Structure **II** 	$^5B_2 \leftarrow {}^4B_2$ Origin = 0.83 eV T = 300 K	1540	1559	0.013	C-C stretch
		1389	1386	0.019	CH_2 scissors
		510	517	0.025	Mo-CCH_2 stretch
	$^3B_2 \leftarrow {}^4B_2$ Origin = 1.36 eV T = 300 K	1389	1395	0.02	CH_2 scissors
		510	553	0.12	Mo-CCH_2 stretch
$MoC_2H_2^-$ Structure **III** 	$^5B_2 \leftarrow {}^4B_4$ Origin = 0.55 eV T = 300 K	499	553	0.11	Mo-η^2 acet stretch
		825	833	0.045	H-CC-H bend
	$^3A_2 \leftarrow {}^4B_4$ Origin = 1.27 eV T = 300 K	499	560	0.375	Mo-η^2 acet stretch
		1569	1543	0.02	C-C stretch
		825	844	0.03	H-CC-H bend
	$^5B_2 \leftarrow {}^6B_2$ Origin = 0.67 eV T = 300 K	815	833	0.15	H-CC-H bend
		489	553	0.28	Mo-η^2 acet stretch
		395	546	0	Out-of-plane bend
		1534	1576	0.04	C-C stretch



[1] Mo-C contracts with decreasing bond angle
[2] Mo-C elongates with decreasing bond angle

	Transition	ω″ (cm^{-1})	ω′ (cm^{-1})	ΔQ (Å·$amu^{1/2}$)	
$MoOC_2H_2^-$ Structure **I** 	$^3A \leftarrow {}^4A''$ Origin = 1.76 eV T = 300 K	883	959	0.12	Mo=O stretch
		623	681	0.33	H a′ out of MoC_2H_2 plane bend
		540	554	0.08	Mo-η^2 acet stretch
		216	232	1	Mo=O bend
	$^5A' \leftarrow {}^4A''$ Origin = 2.63 eV T = 300 K	833	730	0.49	H a′ in MoC_2H_2 plane bend
		540	373	0.9	Mo-η^2 acet stretch
		1531	1798	.09	C-C stretch
		883	933	0.1	Mo=O stretch
$MoOC_2H_2^-$ Structure **II** 	$^3A' \leftarrow {}^4A''$ Origin = 1.70 eV T = 300 K	318	354	0.65	O-Mo-CCH_2 high freq. bend
		850	868	0.22	H-wag
		885	972	0.16	Mo=O stretch
		1401	1362	0.04	CH_2 scissors
	$^5A' \leftarrow {}^4A''$ Origin = 2.16 eV T = 300 K	850	880	0.42	H-wag
		523	440	0.58	Mo-CCH_2 stretch
		318	261	0.78	O-Mo-CCH_2 high freq. bend
		1649	1710	0.08	C-C stretch



	Transition	ω″ (cm^{-1})	ω′ (cm^{-1})	ΔQ (Å·$amu^{1/2}$)	
$MoO_2C_2H_2^-$ Structure **I** 	$^1A_1 \leftarrow {}^2A_1$ Origin = 2.43 eV T = 300 K	284	298	0.31	MoO_2 bend
		916	978	0.19	MoO_2 sym stretch
		835	798	0.13	H a′ in MoC_2H_2 plane bend
		560	538	0.17	Mo-η^2 acet stretch
$MoO_2C_2H_2^-$ Structure **II** 	$^1A' \leftarrow {}^2A_1$ ADE = 2.48 eV VDE = 2.75 eV	Combined low and high freq. modes most active and varied ΔQ until calculated VDE was reproduced, holding ADE at calculated value.